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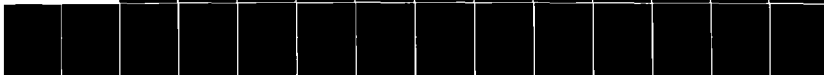
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X-RAY PHOTOELECTRON SPECTROSCOPY OF METAL, METAL OXIDE, AND CAR--ETC(U)  
JAN 80 M UMANA, D R ROLISON, R NOWAK, P DAUM N00018-76-C-0817

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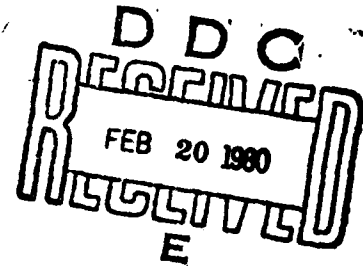
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6 X-Ray Photoelectron Spectroscopy of Metal, Metal Oxide, and  
Carbon Electrode Surfaces Chemically Modified with Ferrocene and Ferricenium,

by

10 M. Umaña, D. R. Rolison, R. Nowak, P. Daum, Royce W. Murray

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ELECTRODE SURFACES CHEMICALLY MODIFIED WITH FERROCENE AND FERRICENIUM

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ABSTRACT

Monomolecular and multilayers of ferrocene derivatives have been deposited on or bonded to electrodes and examined by XPS. In many cases the preparation leaves the modified surface in an oxidized, ferricenium state. Evidence supporting this and possible oxidative mechanisms is discussed.

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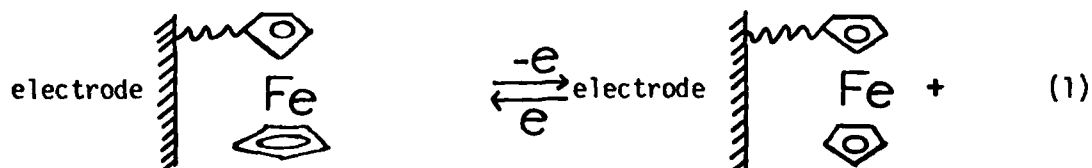
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Since Lane and Hubbard's work (1,2) on olefin chemisorption on Pt and Miller's (3) and ours (4) using covalent bond immobilization chemistry, attaching electrochemically reactive molecules to electrode surfaces has become an active research topic in electrochemistry. The salient characteristic of an electrode surface thus modified is the molecular surface site behavior evident in electrochemical experiments. Thus, an electrode surface to which the reduced state of a molecule is attached exhibits an anodic current flow at a potential centered near the formal potential of the analogous unattached molecule (5), coulometrically transforming the molecule into its oxidized state. This is schematically represented for ferrocene attached to a surface as



The "wiggle" represents the attachment scheme, which permits electron transfer communication between electrode and ferrocene (not necessarily through the "wiggle"). Ferrocene derivatives have been covalently attached to carbon (5-8) and metal oxide (5,8-16) surfaces,

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chemisorbed on Pt (17), and coated on a variety of electrode materials in a polymeric form (6,18-21). Experience thus far indicates that most attachment schemes allow very fast electron transfer although differences in electron transfer rate will undoubtedly appear as kinetic studies progress in this field. Depending (primarily) on the chemical stability of the ferrocene/ferricenium couple, the current response for Reaction 1 persists for many oxidation-reduction cycles, both in the case of attached monomolecular layers and for multilayers. Such stable behavior is attractive for electrocatalytic and other applications.

We regularly use X-ray photoelectron spectroscopy (XPS) to analytically follow surface modification reactions on electrodes (4,22,23). In the course of examining Fe  $2p_{3/2}$  band on immobilized ferrocene surfaces, we noted that some surface attachment procedures left the surface in an oxidized state. This was of interest inasmuch as ferricenium is the less stable state of Reaction 1. Also, for electrodes coated with films of ferrocene polymers, ionic sites in the polymer may influence its swelling by solvent, which is important in the transport of charge through the multilayer polymer film (24). Finally, the electronic conductivity of unswollen ferrocene polymer is enhanced in its mixed valence state (25).

This report describes XPES of ferrocenes immobilized on electrode surfaces using eight different procedures, designated below. Consult the cited literature for further details of preparation and electrochemical behavior.

Procedure A. Vinylferrocene can be polymerized in a radiofrequency Ar plasma discharge to deposit as thin but multimolecular layer films on Pt, glassy carbon, and  $RuO_2$  electrodes (6,18,19,24). Plasma polymerized vinylferrocene, I, resembles conventionally polymerized (radical initiation) vinylferrocene e.g., poly(vinylferrocene), II, in many aspects of electrochemical behavior.

Procedure B. Films of poly(vinylferrocene), II, on Pt are prepared by evaporation of a droplet of a dilute solution of II spread over the electrode surface (26).

Procedure C. Ferrocene polymers I and II are electrochemically precipitated as ferricenium onto Pt surfaces by anodic electrolysis in  $\text{CH}_2\text{Cl}_2$  solution (19,21).

Procedure D. Reactive "oxide free" carbon surfaces are generated by mechanical fracture (abrasion) of glassy carbon surfaces (GC) under a puddle of a concentrated solution of vinylferrocene (6,27) in a  $\text{N}_2$  glovebox.

Procedure E. Procedure D is carried out using cyanuric chloride solution. This abraded surface, to which cyanuric chloride has become bound, is washed with a solvent and coupled with aminophenylferrocene (27).

Procedure F. Thin films of oxides on Pt and Au surfaces are reacted with solutions of [1,1'-ferrocenediyl]dichlorosilane (11-13).

Procedure G. Glassy carbon,  $\text{RuO}_2$ , and Pt/PtO surfaces are reacted with 3-(2-aminoethylamino)propyltrimethoxysilane (en silane) or 4-(methyldichlorosilyl)butyryl chloride (BuCl silane). The rinsed alkylamine or acid chloride functionalized surface is then coupled to a carboxylic acid or aminoferrocene derivative, respectively (9,10).

Procedure H.  $\text{RuO}_2$  electrodes are activated by reaction with  $\text{SOCl}_2$  for coupling to aminophenylferrocene (28).

Procedures D, E, G, and H are generally considered to yield monolayers or submonolayers of covalently immobilized ferrocenes. Procedures A, B, C, and F yield ferrocene polymer-coated surfaces, e.g., multiple layers of ferrocene sites. Reaction 1 on the multilayer ferrocene surfaces proceeds by charge transport through the polymer matrix as well as charge transfer to the electrode material, both involving intermediacy of the ferricenium state.

## EXPERIMENTAL

X-ray photoelectron spectra were obtained on a DuPont Model 650B electron spectrometer equipped with Mg anode and microprocessor unit for data acquisition and storage. Binding energies are corrected for charging relative to C 1s taken as 285.0 e.v. Charging corrections were small (1 - 2 e.v.) for powdered ferrocene and ferricenium model compounds (determined on sticky tape), and ferrocene polymer films on electrodes, and were very small for ferrocene monolayer films on conducting electrodes. Authentic poly(vinylferrocene) was a gift from M. Wrighton (M.I.T.).

Ferrocene electrode surfaces were prepared as described in the cited literature or as specified in Results.

## RESULTS AND DISCUSSION

Model Ferrocene and Ferricenium Compounds. The XPS binding energy for the  $2p_{3/2}$  orbital of iron in ferrocene is 707.9 e.v. (29) relative to C 1s at 285.0 e.v. While the  $2p_{3/2}$  binding energy varies for substituted ferrocenes, Table I, the range of substituent shifts is only ca. 1.2 e.v. Ferricenium  $2p_{3/2}$  B.E. exceed those of structurally similar ferrocenes by 2 - 4 e.v., as illustrated by the mixed valence entries 9, 13, and 14, Table I.

Ferrocene and ferricenium states are additionally distinguishable by  $2p_{3/2}$  band shapes. The ferrocene band FWHM observed with our spectrometer was typically 2.0 e.v., whereas that for ferricenium was substantially larger, 5 - 6 e.v. The broad ferricenium  $2p_{3/2}$  has been previously observed and attributed to exchange interactions (31). Ferricenium binding energies are . . . . . much less precise because of the broad peaks.

No examples of obvious X-ray beam damage were encountered for either ferrocene or ferricenium compounds. Nor were any unusual effects noted in measurements on samples of authentic poly(vinylferrocene), Figure 1A. None



of the ferrocene materials showed a notable ferricenium impurity. The model compound results show that XPS readily distinguishes ferrocene and ferricenium states on modified electrode surfaces. However, we also should note that the ca. 711 e.v. B.E. of ferricenium is similar to that of other Fe(III) compounds.

Procedure A. Electrodes Coated with Films of RF Plasma Polymerized Vinylferrocene, I. We have presented details of this procedure elsewhere (18,19). Briefly, a charge of solid vinylferrocene monomer is positioned 0.5 - 2 cm. away from the electrode surface to be coated in a vacuum chamber, which is evacuated and backfilled with 200 - 250 mtorr Ar. A ca. 10 watt plasma discharge (purple) is initiated and continued for several seconds to minutes, the chamber reevacuated for ca. 20 minutes, backfilled with air, and the coated electrodes removed for XPS or electrochemical examination. Three or four electrodes can be coated at one time. Electrochemical stability is improved by aging 1-2 weeks in air.

The ferrocene $\rightarrow$ ferricenium Reaction 1 for films of I is illustrated by the cyclic voltammetry of Figure 2, which has an appearance indicating fast (non-equilibrium) charge transport through this particular sample. The acetonitrile solvent swells but does not dissolve I. The reaction corresponds to charge transport through  $6.1 \times 10^{-9}$  mole/cm.<sup>2</sup>, or approximately 20 layers, of ferrocene sites. The thickness of films of I varies ( $1 - 300 \times 10^{-10}$  mole/cm.<sup>2</sup>) with plasma deposition time and with electrode material. Data cited here are mostly for 3 minute depositions in Geometry B (19), yielding coverages in the range  $1 - 10 \times 10^{-9}$  mole/cm.<sup>2</sup>.

During early plasma deposition experiments on glassy carbon and Pt electrodes (19), XPS spectra were typically as in Figure 1B, where Fe 2p<sub>3/2</sub> binding energy (Table I, Expt. 1,2) and peak broadness indicate the iron in the films is in an oxidized state. Films prepared with ferrocene as monomer

(Expt. 3) were similarly oxidized. Subsequently, following several adjustments, we were able to produce (18,26) mixed valence films of I which contain mostly ferrocene with 10-40% oxidized iron, judging by relative band intensity (Figure 1C), again irrespective of electrode material, Table II, Expts. 4 - 6. Soaking these latter films of I in solutions of reducing agents, Expts. 7,8, reduces the relative intensity of the 711 e.v. band, Figure 1F, arguing that the high binding energy  $2p_{3/2}$  band is a genuine Fe(III) oxidation state and is not associated with energy loss satellites (11). Control Expts. 9 and 10 show some loss in ferrocene intensity relative to the 711 e.v. band, so the Expt. 7,8 results are not simply a consequence of the acidity of the reducing solution.

The oxidation of the deposited films of I is primarily associated with chemical effects of the radiofrequency Ar plasma. Deliberate contamination of the plasma with oxygen during deposition (Expts. 11,12) produced no particular change in the film's XPS (compare Figure 1D to 1C), whereas re-exposure of a specimen from Expt. 11 to an oxygen-free Ar plasma (in the absence of an additional charge of monomer) clearly promotes oxidation (Expt. 13, Figure 1E). In another experiment, a film of II, poly(vinylferrocene), prepared by Procedure B from toluene and initially by XPES entirely in the ferrocene state, was exposed to the Ar plasma to produce a spectrum similar to Figure 1E. The greater effective plasma exposure and oxidation in Expts. 1, 2, as compared to Expts. 4-6, was apparently associated with the smaller charges of monomer and greater electrode-monomer separation in the former. It seems that plasma oxidation is countered by a rapid film deposition by minimizing the plasma exposure required to achieve a certain film thickness. Rapid deposition, up to a point, is promoted by proximity of the electrode surface to a sufficient supply of plasma-heated solid vinylferrocene monomer

to maintain a high local vapor pressure of polymerizing monomer.

The properties of films of I are qualitatively similar to those of II, but can be observed to vary with the extent of plasma oxidation. In particular, the transport of charge through I during its electrochemical oxidation and reduction is slower for the more extensively plasma oxidized films. Charge transport rate limitations in films of I prepared as in Expt. 2 were often observable at room temperature (19); temperatures of  $-70^{\circ}\text{C}$  were required to provoke similar control in films of like ferrocene coverage prepared as in Expt. 6, (18). Secondly, for films of I deposited on Pt, the ratio of (total) Fe  $2p_{3/2}$  and Pt  $4f$  intensities associated with a given quantity of voltammetrically reactive ferrocene (e.g. Figure 2) is (i), in general larger when plasma oxidation is extensive as in Figure 1B, and (ii) for low levels of plasma oxidation (e.g. Figure 1C) is similar to that observed in the silyl-ferrocene polymer of Procedure F (11).

The solubility properties of I also vary; extensively plasma oxidized films of I resist dissolution in solvents such as toluene and  $\text{CH}_2\text{Cl}_2$  in which films like that of Figure 1C slowly dissolve (leaving a residue of the oxidized form, Expts. 14,15) and in which II readily dissolves. Finally, samples of plasma oxidized I harvested from glass slides placed in the plasma chamber (19) have the empirical formula  $\text{FeC}_{10.9}\text{H}_{12.6}\text{O}_{2.1}$ .

The binding energy of the oxidized iron peak agrees with that expected for the ferricenium state, and results such as observing ferrocene-ferricenium electrochemistry with films initially exhibiting no 708 e.v. XPS band at all requires that ferricenium states exist and contribute to the broad 711 e.v. band. The above and other data strongly suggest, on the other hand, that extensive plasma leads to additional oxidative steps, producing a non-electrochemically reactive organoiron(III) species having binding energy indistinguishable from ferricenium. This species remains firmly affixed to the polymer matrix.

In the following Procedures, we have no reason to suspect that species other than ferricenium contribute to the 711 e.v. band.

Procedure B. Electrodes Coated with Poly(vinylferrocene), II, by Solvent

Evaporation. Films of II can be obtained quite simply by slowly evaporating a few (1-5) microliters of a 1 mg/10 ml solution in a volatile solvent spread over the electrode surface. These films exhibit electrochemical properties in aqueous media quite similar to those of I (26), but due to the topological roughness (readily seen in 700x scanning electron microscopy) associated with uneven evaporation, typically only 50-80% of the material known to be deposited reacts electrochemically. (Spin coating would be a superior method but has not been used for II).

The oxidation state of Procedure B films of II depends on the evaporating solvent. Evaporation from toluene yields a principally ferrocene surface (Figure 3A, Expts. 16,17) whereas  $\text{CH}_2\text{Cl}_2$  solutions (Figure 3B, Expts. 18,19) produce principally oxidized films. This effect can be understood in terms of ferrocene photochemistry in chlorinated solvents (32,33), in which a dissociative charge transfer reaction yields chloride, ferricenium, and a solvent radical. Since our droplet evaporation experiments were conducted in light, some photolytically produced ferricenium is to be expected and the 711 e.v. peak is reasonably interpreted as ferricenium. Total exclusion of light during deposition from  $\text{CH}_2\text{Cl}_2$  yields only the 708 e.v. band, proving the photochemical explanation. Not all samples showed the nearly total conversion of II to ferricenium evident in Figure 3B; some showed ~ 50% ferrocene due presumably to a different extent of photolysis.

Procedure C. Electrochemical Precipitation of I and II from  $\text{CH}_2\text{Cl}_2$ . Merz and Bard (21) exploited the low solubility of poly(vinylferricenium) in  $\text{CH}_2\text{Cl}_2$  to oxidatively deposit films of it from solutions of II on an anodically potential-stated Pt electrode. The coated electrode is subsequently used in acetonitrile

solvent to observe cyclic voltammograms representing Reaction 1. This experiment is also possible (19) with harvested samples of plasma polymerized vinylferrocene I dissolved in  $\text{CH}_2\text{Cl}_2$ .

The expected ferricenium state of Pt anodes removed from  $\text{CH}_2\text{Cl}_2$  solutions of I or II is confirmed by XPS in Expts. 20,21 only a broad 711 e.v. peak is observed. In view of the Procedure B results, however, it is not straightforward that the ferricenium on these surfaces is produced exclusively by electrochemical oxidation in  $\text{CH}_2\text{Cl}_2$ ; photochemistry may play a secondary role.

Our usual procedure in cyclic voltammetric studies of ferrocene films involves both initiation and termination of the experiment with the working electrode held at 0 volts vs. S.C.E. which should place the electrode in the ferrocene state. Following using this procedure in acetonitrile with films of I or II deposited by the Merz-Bard experiment, then rinsing ( $\text{CH}_3\text{CN}$ ) and air drying, we find that XPS shows only the ferricenium peak (Figure 3C). These films are, unexpectedly, readily re-oxidized.

#### Procedure D. Abrasion of Glassy Carbon in Presence of Vinylferrocene.

Following the (oversimplified) view that cleavage across a basal plane produces a radical surface prone to olefin cycloaddition reactions (34), we established that mechanical abrasion of glassy carbon in the presence of vinylferrocene stably attaches an electroactive ferrocene moiety to the carbon (6). Ferrocene electrochemistry or XPS is not produced by simply soaking glassy carbon in vinylferrocene solutions or by abrasion under ferrocene/benzene solutions, so the fractured surface plus vinyl substituent are essential to attachment. Electrochemically-measured coverages are consistently at the monolayer or sub-monolayer level (e.g.,  $1 - 3 \times 10^{-10}$  mole/cm.<sup>2</sup>). We have uncovered no clear evidence of homopolymer initiation of vinylferrocene by the reactive carbon surface although this remains a troublesome point (27).

Since coverage is low, signals are less intense, but XPS spectra

consistently show that the surface is in a ferricenium state, Figure 3D and Expt. 22. Furthermore, the carbon surface remains in the ferricenium state following electrochemical experiments, in  $\text{CH}_3\text{CN}$ , in which the electrode is disconnected at 0 volt vs. S.C.E.

Procedure E. Surface Coupling with Cyanuric Chloride. Kuwana and coworkers (7,8,35,36) have employed the reaction of cyanuric chloride with metal oxide and carbon surfaces to couple other reagents to these surfaces. A sequence of reaction steps calculated to maximize surface hydroxyl was used to prepare the carbon surfaces for the cyanuric chloride reaction.

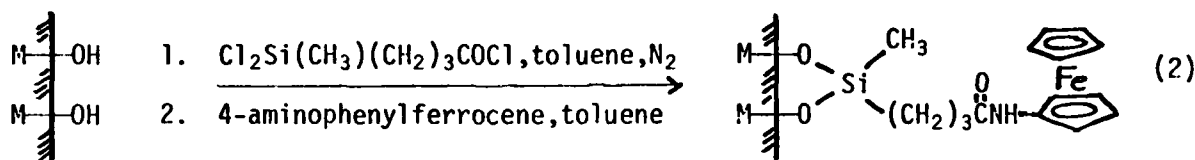
We have abraded glassy carbon in the presence of cyanuric chloride to see if this simpler procedure can promote cyanuric chloride binding. Based on well-developed cyclic voltammetric waves observed after reacting these (rinsed) samples with aminophenylferrocene, the immobilized ferrocene coverages was approximately doubled by the abrasive procedure, as compared to simple soaking in cyanuric chloride. In both cases, (Expts. 23,24), XPS showed the ferrocene was in its reduced form. The aminophenylferrocene coverage in the abrasion experiment was  $7.7 \times 10^{-10}$  mole/cm.<sup>2</sup> (on 50th potential cycle) which compares favorably with the reported  $2 \times 10^{-10}$  mole/cm.<sup>2</sup> (7). The details of the cyanuric chloride coupling reaction with the fractured carbon are unknown.

Procedure F. Reaction of Metal Oxide Electrode Surfaces with

[1,1'-ferrocenediyl]dichlorosilane. This reaction produces a polymeric, mixed valence surface, (Expts. 25,26, Figure 3E), as described in a previous report (11). The XPS-examined electrode specimens had been subjected to prior electrochemical characterization, terminating the experiment at a ferrocene potential, yet ferricenium was present after drying and shipment from MIT to UNC.

Procedure G. Coupling of Ferrocene Derivatives to Silanized Metal Oxide Electrodes. Oxide electrodes form stable MOSi bonds with chloro- and

alkoxysilanes (4) and thus immobilized organosilane reagents can be coupled with ferrocene derivatives to form bonded monolayers. This is illustrated for 4-(methyldichlorosilylbutyryl)chloride by reaction (10):



where M can be Sn, Ru, Pt, or glassy carbon. An analogous coupling scheme was based on 3-(2-aminoethylamino)propyltrimethoxy silane and ferrocene carboxylic acids (9). XPS results are given in Expts. 27-29 (Figure 3H) and Expts. 30,31 (Figure 3G), respectively. The usual state is ferrocene with minor ferricenium present, but on occasion a 711 e.v. band consistent with ferricenium is predominant (Expt. 31).

Procedure H. Coupling of Ferrocene Derivatives to RuO<sub>2</sub> Activated With Thionyl Chloride. Recently we have activated metal oxide electrodes with SOCl<sub>2</sub> for coupling-immobilization of amines (28). Thus, activated RuO<sub>2</sub> binds aminophenylferrocene, through the linkage Ru-O-SO-NH-, and exhibits ferrocene XPS, Expt. 32, Figure 3F, and modestly stable ferrocene electrochemistry. The predominant coupling product is ferrocene but small peaks for ferricenium also appear.

## DISCUSSION

It has been tacitly assumed in the electrode modification literature that oxidation state changes do not occur during immobilization procedures. The present results show this to be a poor assumption for ferrocenes. Interpretation of the broad 711 - 712 e.v. Fe 2p<sub>3/2</sub> bands observed above as ferricenium is reasonable given i) agreement of its binding energy with that of known ferricenium compounds (Table I), ii) its ubiquitous presence on ferrocene surfaces

prepared by very different procedures, making it less likely to be an Fe(III) ferrocene decomposition product (we have discussed plasma oxidized films as an exception to this), and iii) its wide variation in intensity relative to ferrocene (which rules out an energy loss satellite explanation). The ferricenium state probably impacts on the useful shelf life between electrode preparation and electrochemical use, but we have not studied this systematically.

The nature of the oxidation leading to the ferricenium surfaces of course varies with electrode preparation procedure. In Procedure A plasma oxidation was implicated, in Procedure B photochemistry in chlorinated solvent was the source, in Procedure C the electrochemical pathway deliberately produced a ferricenium layer, and in Procedures F, G, and H the acidity of the coupling reaction medium (via the acid halides) probably was important.

In Procedure D the oxidative mechanism is less obvious. We will speculate on an electron exchange reaction between surface ferrocene and the quinone sites which exist (39) on carbon surfaces exposed to air. The relative  $E^\circ$  values of these couples are such that this can occur, and this mechanism could maintain the electrode surface in a ferricenium/hydroquinone state when in contact with moist air, irrespective of prior electrochemistry.

Other oxidation mechanisms operate to return ferrocene states to ferricenium ones in  $\text{Et}_4\text{N}^+\text{ClO}_4^-/\text{CH}_3\text{CN}$  media after electrochemical examination. This was seen in electrodes prepared in Procedures C and F. The chemistry involved in this unusual effect is not known.

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TABLE I

BINDING ENERGY (eV) OF IRON  $2p_{3/2}$  ORBITALS IN FERROCENE DERIVATIVES

		<u>Fe(II)</u>	<u>Fe(III)</u>
1 <sup>a</sup> .	ferrocene	707.9	
2 <sup>b,c</sup> .	aminophenylferrocene	708.2	
3.	vinylferrocene	708.4	
4 <sup>c</sup> .	ferrocene-1,1'-dicarboxylic acid	708.6	
5 <sup>c</sup> .	ferrocenecarboxylic acid	708.8	
6.	poly(vinylferrocene)	708.8	
7 <sup>d</sup> .	[trimethylaminomethylferrocene] <sup>+</sup> I <sup>-</sup>	708.6	
8 <sup>d</sup> .	[trimethylaminomethylferrocene] <sup>+</sup> PF <sub>6</sub> <sup>-</sup>	709.1	
9 <sup>c,e</sup> .	[1,1'-ferrocenediyl]dichlorosilane	708.3	711
10 <sup>f</sup> .	[dimethylferricenium] <sup>+</sup> I <sub>3</sub> <sup>-</sup>		710.6
11 <sup>f</sup> .	[ferricenium] <sup>+</sup> I <sub>3</sub> <sup>-</sup>		710.1
12 <sup>c</sup> .	[(CH <sub>3</sub> ) <sub>3</sub> SiC <sub>p</sub> ] <sub>2</sub> Fe <sup>+</sup> BF <sub>4</sub> <sup>-</sup>		710.6
13 <sup>g</sup> .	[biferrocene(II),(III)] <sup>+</sup> picrate <sup>-</sup>	707.9	711.1
14 <sup>h</sup> .	KFe[Fe(CN) <sub>6</sub> ]	708.5	712.9

a. Ref. 29.

b. Ref. 9.

c. Ref. 11.

d. Courtesy J. R. Lenhard, University of North Carolina.

e. hydrolyzed, polymeric sample.

f. Courtesy Prof. M. S. Brookhart, University of North Carolina.

g. Ref. 6.

h. Prussian blue, corrected for charging effect, Ref. 30.

TABLE II

## XPS BINDING ENERGIES OF FERROCENE ELECTRODES

Pro- cedure	Expt. #	Sub- strate	COMPOUND	SURFACE PREPARATION	B.E. OF Fe 2p <sub>3/2</sub> ORBITAL [eV] <sup>f</sup>
A	1	GC	vinylferrocene	RF plasma polymerization, early experiments <sup>b</sup>	- 711.4
A	2	Pt	vinylferrocene	RF plasma polymerization, early experiments <sup>b</sup>	- 711.3
A	3	GC	ferrocene	RF plasma polymerization, early experiments	- 711.6
A	4	GC	vinylferrocene	RF plasma polymerization <sup>c</sup>	708.7* 711.5
A	5	RuO <sub>2</sub>	vinylferrocene	RF plasma polymerization <sup>c</sup>	708.7* 712.0
A	6	Pt	vinylferrocene	RF plasma polymerization <sup>c</sup>	708.9* 712.2
A	7	Pt	sample from Expt. 6	reduced with 10% Aq. ascorbic acid (pH 2) (9: hours)	708.8 -
A	8	Pt	sample from Expt. 6	reduced with 10% Aq. NaHSO <sub>3</sub> (pH 3.6)	709.1 -
A	9	Pt	sample from Expt. 6	soaked in Aq. H <sub>2</sub> SO <sub>4</sub> (pH 2) (117 hours)	708.7 712.3*
A	10	Pt	sample from Expt. 6	soaked in Aq. acetic acid (pH 3.6)	708.8 711.7*
A	11	Pt	vinylferrocene	RF plasma polymerization from Ar/O <sub>2</sub> plasma	709.1* 712.3
A	12	GC	vinylferrocene	RF plasma polymerization from Ar/O <sub>2</sub> plasma	709.3* 712.8
A	13	Pt	sample from Expt. 11	re-exposed to Ar plasma (3 minutes)	709.1 712.0
A	14	RuO <sub>2</sub>	sample from Expt. 5	soaked in toluene	- 710.7
A	15	RuO <sub>2</sub>	sample from Expt. 5	soaked in CH <sub>2</sub> Cl <sub>2</sub>	708.7 711.6*
B	16	Pt	poly(vinylferrocene), 11	evaporated toluene solution, exposed to daylight <sup>d</sup>	709.2 -
B	17	GC	poly(vinylferrocene), 11	evaporated toluene solution, exposed to daylight <sup>d</sup>	709.5 -
B	18	Pt	poly(vinylferrocene), 11	evaporated CH <sub>2</sub> Cl <sub>2</sub> solution, exposed to daylight <sup>d</sup>	- 711.4
B	19	SiO <sub>2</sub>	poly(vinylferrocene), 11	evaporated C <sub>2</sub> H <sub>5</sub> Cl <sub>2</sub> solution, exposed to daylight	709.1 711.4*

C	20	Pt	poly(vinylferrocene), <u>II</u>	electrochemical precipitation from $\text{CH}_2\text{Cl}_2$ solution <sup>e</sup>	-	711.4
C	21	Pt	plasma polymerized vinylferrocene, <u>I</u>	electrochemical precipitation from $\text{CH}_2\text{Cl}_2$ solution <sup>e</sup>	-	711.3
D	22	GC	vinylferrocene	carbon abraded under concentrated vinylferrocene/benzene solution, under $\text{H}_2$	-	711.4
E	23	GC	aminophenylferrocene	carbon abraded under concentrated cyanuric chloride/benzene solution, reacted with aminophenylferrocene in $\text{CH}_3\text{CN}$	708.9	-
E	24	GC	aminophenylferrocene	carbon soaked in concentrated cyanuric chloride/benzene solution, reacted with aminophenylferrocene in $\text{CH}_3\text{CN}$	708.9	-
E	25	Pt/PtO	[1,1'-ferrocenediyl]-dichlorosilane	reaction with surface metal hydroxide and polymerization <sup>9</sup>	707.9*	711.4
F	26	Au/Au <sub>2</sub> O <sub>3</sub>	[1,1'-ferrocenediyl]-dichlorosilane	reaction with surface metal hydroxide and polymerization <sup>9</sup>	707.9*	711.2
G	27	RuO <sub>2</sub>	aminophenylferrocene	amide couple to oxide surface silanized with <u>BuCl</u> silane <sup>h</sup>	708.1	-
G	28	RuO <sub>2</sub>	aminoferrrocene	amide couple to oxide surface silanized with <u>BuCl</u> silane <sup>h</sup>	708.1*	711.3
G	29	GC	aminophenylferrocene	amide couple to oxidized carbon surface silanized with <u>BuCl</u> silane <sup>i</sup>	708.9*	711.5
G	30	Pt/PtO	ferrocenephenylacetic acid	amide couple to oxide surface silanized with <u>en</u> silane <sup>j</sup>	708.6	-
G	31	Pt/PtO	ferrocenephenylacetic acid	amide couple to oxide surface silanized with <u>en</u> silane	-	711.4
H	32	RuO <sub>2</sub>	aminophenylferrocene	react aminophenylferrocene with oxide surface activated with $\text{SOCl}_2$ <sup>k</sup>	708.4*	711.5

TABLE II Footnotes

a. While data are cited for single experiments, all have been repeated at least in duplicate. Average deviation of ferrocene B.E. is  $\pm 0.3$  e.v. for Procedures A-C,  $\pm 0.1$ - $0.2$  for others; for ferricinium  $\pm 0.4$  e.v. for Procedures A-C.

b. Preparation and electrochemical properties of films of I prepared in these experiments are described in reference 19.

\*Predominant peak

- c. Electrochemical properties of films of I, mostly ferrocene, are discussed, at low temperature in butyronitrile in reference 19, and in water, water/ethanol, and acetonitrile in reference 24.
- d. Evaporation of 5  $\mu$ l. of a 1.1 mg solution of II in 10 ml of the solvent on a 0.3  $\text{cm}^2$  electrode disk.
- e. A Pt disk electrode is potentiostated at +0.7 volt vs. S.C.E. in a several mM solution of I or II for a few minutes, disconnected, rinsed with  $\text{CH}_2\text{Cl}_2$  and then  $\text{CH}_3\text{CN}$ .
- f. See reference 6 for details.
- g. Data from reference 11.
- h. See reference 10 for details.
- i. Unpublished results, R. Nowak and K. Willman, UNC, 1978.
- j. Data from reference 9.
- k. Unpublished results, K. Kuo, UNC, 1979.

## Figure Legends

Figure 1. Fe  $2p_{3/2}$  XPS spectra demonstrating Fe(II) and Fe(III) states in polymeric vinylferrocenes under stated experimental conditions;

- Curve A: powdered polyvinylferrocene (PVF) prepared using AIBN as initiator and standard solution polymerization conditions;
- Curve B: RF plasma polymerized vinylferrocene film deposited on GC, early experimental conditions (Expt. 1);
- Curve C: RF plasma polymerized vinylferrocene film deposited on Pt, low damage experimental conditions (Expt. 6);
- Curve D: Vinylferrocene polymerized in Ar/O<sub>2</sub> plasma deposited on Pt;
- Curve E: Vinylferrocene polymer film on Pt prepared as in D, re-exposed to Ar plasma in the absence of monomer;
- Curve F: Expt. 6, RF plasma polymerized vinylferrocene film on Pt soaked in 10% aqueous NaHSO<sub>3</sub> for three days.

Figure 2. Cyclic voltammetry of RF plasma polymerized vinylferrocene film on GC. 0.1 M Et<sub>4</sub>NCIO<sub>4</sub> in CH<sub>3</sub>CN; 0.1 volt/second; room temperature.

Figure 3. Fe  $2p_{3/2}$  XPS spectra for various ferrocene species deposited, evaporated, abraded or bonded to electrodes under stated experimental conditions;

- Curve A: Evaporation on Pt from a toluene solution of 0.5 microgram authentic polyvinylferrocene;
- Curve B: Evaporation on Pt from 0.5 microgram authentic polyvinylferrocene in CH<sub>2</sub>Cl<sub>2</sub>, ambient light and temperature;
- Curve C: Authentic PVF electrochemically deposited on Pt from 0.1 M Bu<sub>4</sub>NCIO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> solution, spectrum after electrochemical cycling;
- Curve D: Abrasion of GC in an inert atmosphere under a concentrated benzene solution of vinylferrocene;

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- Curve E: Au silanized with  $\text{Fe}(\text{cp})_2\text{SiCl}_2$  (from ref. 11);
- Curve F:  $\text{RuO}_2$  activated with  $\text{SOCl}_2$  then reacted with aminophenylferrocene;
- Curve G: Pt silanized with en silane (3-(2-aminoethylamine)propyltrimethoxy silane) coupled to ferrocenylphenylacetic acid via DCC (dicyclohexylcarbodiimide);
- Curve H: GC silanized with BuCl silane (4-(methyldichlorosilyl)butyryl chloride reacted with aminophenylferrocene.
- . . . . .



